New High-Energy Electrochemical Couple for Automotive Applications

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Argonne National Laboratory

DOE merit review

June 8-12, 2015

Project ID: ES208

Overview

Timeline

- Start - October 1st, 2013.
- Finish - September 30, 2015.
- 60% Completed

Barriers

- Barriers addressed
  - High energy (>200wh/kg)
  - Long calendar and cycle life
  - Abuse tolerance

Budget

- Total project funding
  - DOE share: 2500K
- Funding received in FY13: 1250K
- Funding for FY14: $1250K

Partners

- Project lead: Khalil Amine
- Interactions/ collaborations:
- **X. Q. Yang (BNL)** **diagnostic of FCG cathode and SEI of Si-Sn composite anode**
- **G. Liu (LBNL) development and optimization of conductive binder for Si-Sn composite anode**
- **ECPRO: provide baseline cathode material**
- **Utah University: provide facility to scale up the baseline Si-Sn composite anode for baseline cell**
- **Andy Jansen & Polzin, Bryant (ANL) fabrication of baseline cell**
- **Paul Nelson (ANL) design of cell using BatPac**

Relevance and project Objectives

- Objective: develop very high energy redox couple (250wh/kg) based on high capacity full gradient concentration cathode (FCG) (230mAh/g) and Si-Sn composite anode (900mAh/g) with long cycle life and excellent abuse tolerance to enable 40 miles PHEV and EVs

- This technology, If successful, will have a significant impact on:
  - *Reducing battery cost and expending vehicle electrification*
  - *Reduce greenhouse gases*
  - *Reduce our reliance on foreign oil*

Milestones

- March 2015:
  - Improve efficiency of SiO-SnCoC anode to over 80% (completed)

- August 2015:
  - Finalize the Optimization of the processing of SiO-SnCoC-MAG to get uniform electrodes and demonstrate up to 500 cycles of SiO-SnCoC-MAG using new LiPAA binder (on schedule)

- September 2015:
  - Optimize and scale up of Improve further FCG cathode with 230mA/g at 4.5V and demonstrate 250wh/kg at the cell level using improved FCG cathode and SiO-SnCoC-MAG anode (on schedule).

Approach

ANODES

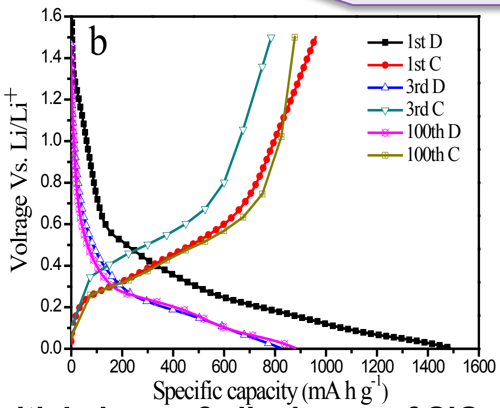
$SiO\text{-}Sn_yCo_{1-x}Fe_xC_z$ composite coupled with conductive binder

ELECTROLYTES

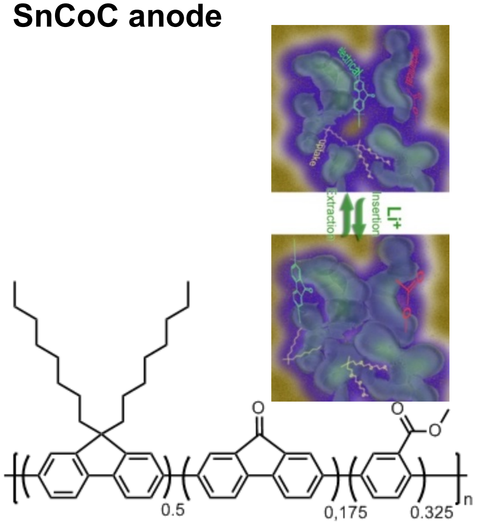
High voltage electrolytes with additives to stabilize interface of cathode and anode

CATHODES

Full Gradient concentration (FCG) $LiNi_xMn_yCo_zO_2$ with high concentration of Mn at the surface of the particle

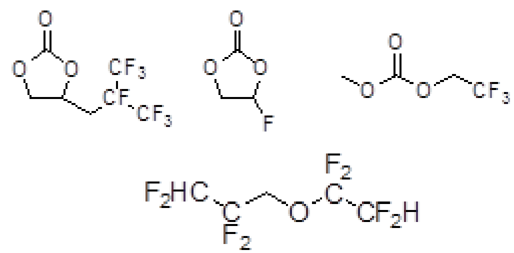


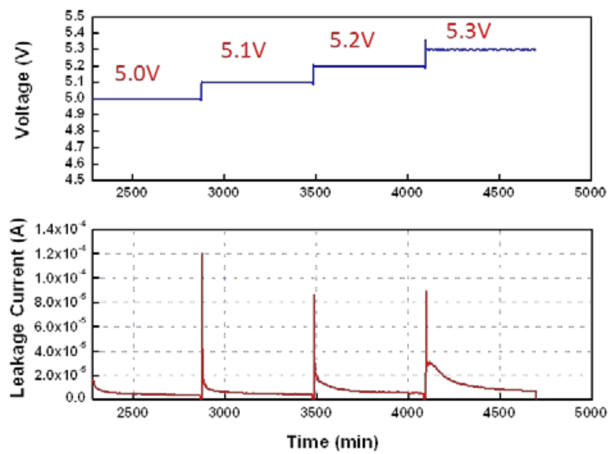
Initial charge & discharge of SiO-SnCoC anode



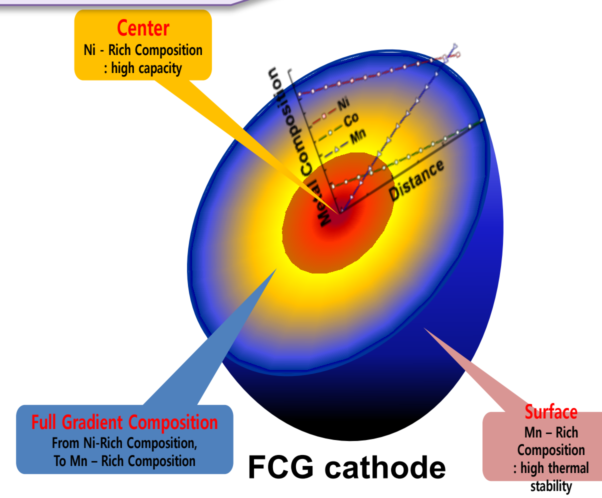
Conductive binder

Fluorine based electrolyte with additives:

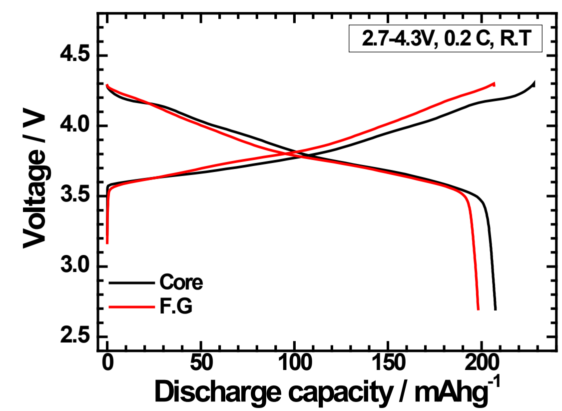




Floating test at different voltages of $LiNi_{0.5}Mn_{1.5}O_4/Li_4Ti_5O_{12}$ Cell using fluorinated electrolyte



FCG cathode



Initial charge & discharge of FCG cathode

Technical accomplishments

- Optimize the process of making FCG cathode and demonstrate capacity as high as 210mAh/g with 2.7 tap density
- Characterize the FCG material using soft and hard X-ray in collaboration with BNL
- Scale up FCG cathode to 1Kg level for electrode making using CAMP facility at Argonne
- Demonstrate that capacity, cycle life and safety of FCG (6:2:2) cathode outperform that of NMC (6:2:2) baseline.
- Improve the efficiency of SiO-Sn_{30} $Co_{30}C_{40}$ anode to 81% by Developing SiO-Sn_{30} $Co_{30}C_{40}$ –MAG graphite composite formulation and scale up the new composite to 1Kg level.
- Develop a suitable binder LiPAA that work well with the new composite anode for Gen 1 cell fabrication
- Continue to improve the performance of conductive binder in collaboration with LBNL

FCG Cathode development approach

1. **Design of full concentration gradient cathode material**
2. **Preparation of full concentration gradient (FCG) precursor via CSTR Co-precipitation with optimized condition**
3. **Calcination of FCG cathode with optimized condition**
4. **Physical characterization**
5. **Electrochemical evaluation**

FCG material design

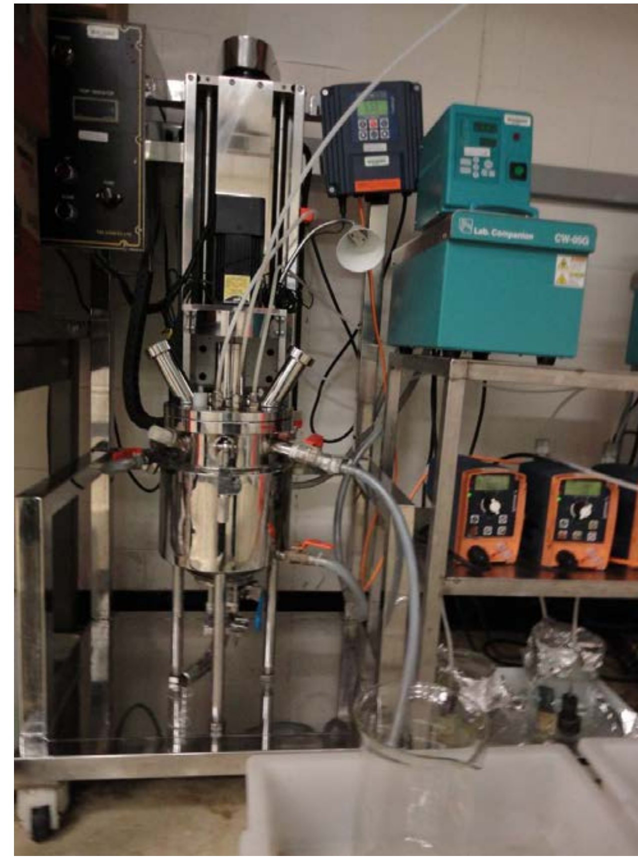
Optimize the precursor

Optimize the calcination

Characterization (XRD, SEM, TEM)

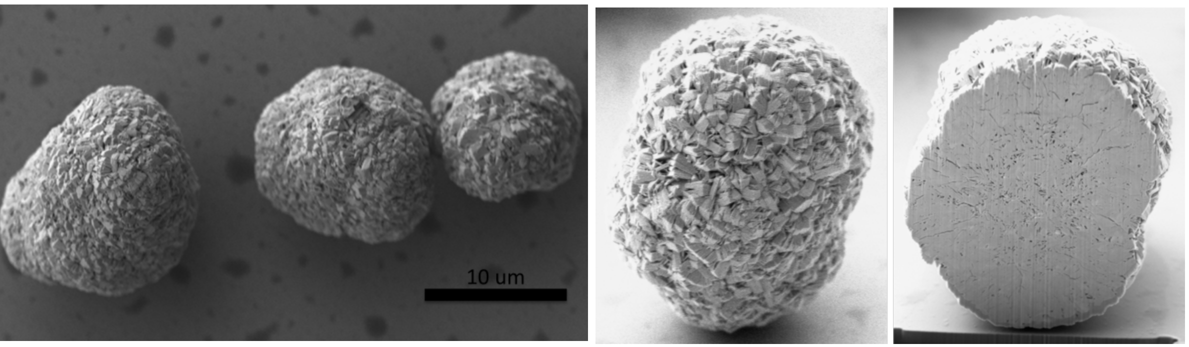
Electrochemical evaluation (coin cell)

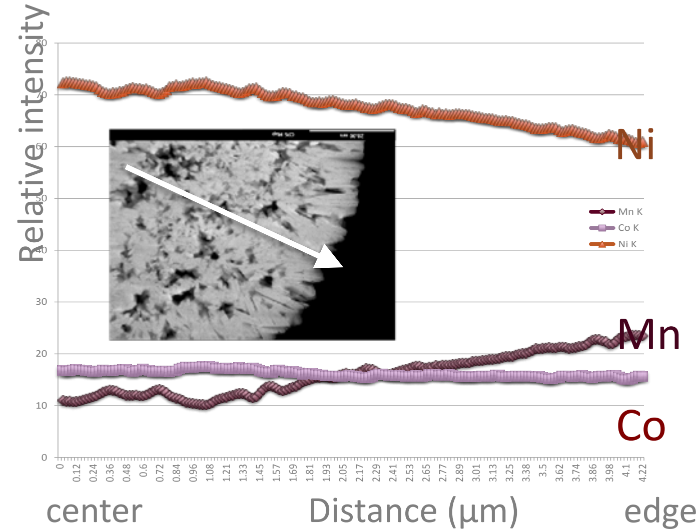
CFF for pouch cell evaluation



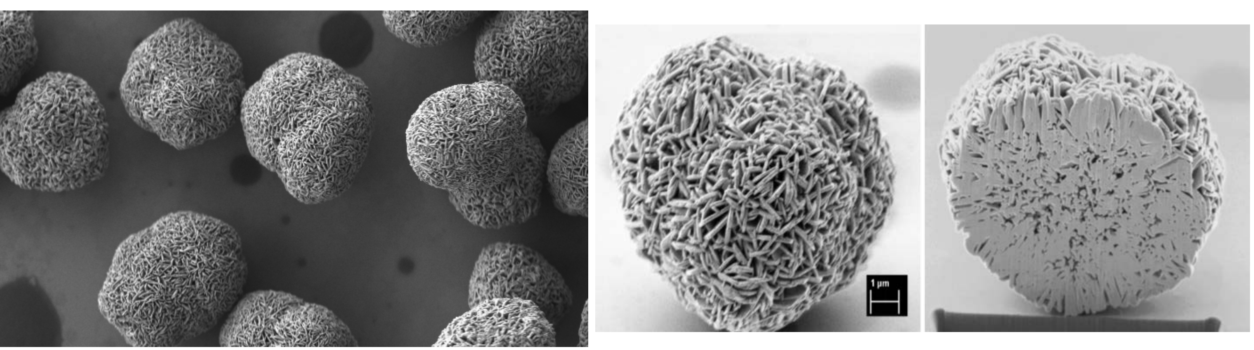
Reactor Setup

Characteristics of FCG gradient precursor & final active material made from hydroxide process after optimization





$Ni_{0.6}Co_{0.2}Mn_{0.2}(OH)_2$



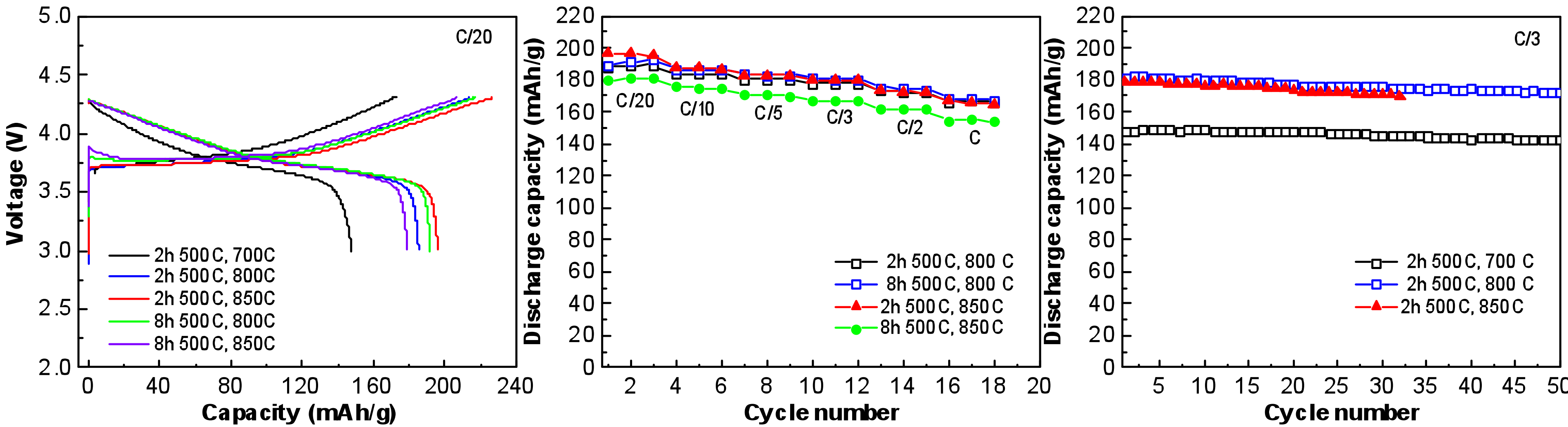
The average composition:
$\sim LiNi_{0.6}Co_{0.2}Mn_{0.2}O_2$
Outer: $\sim LiNi_{0.46}Co_{0.23}Mn_{0.41}O_2$
Inner: $\sim LiNi_{0.8}Co_{0.1}Mn_{0.1}O_2$

FCG (6:2:2) : $LiNi_{0.6}Co_{0.2}Mn_{0.2}O_2$

High tap density: 2.7 g/cc
particle distribution: D50=11.64 um

Main impact factors on the performance of FCG cathode

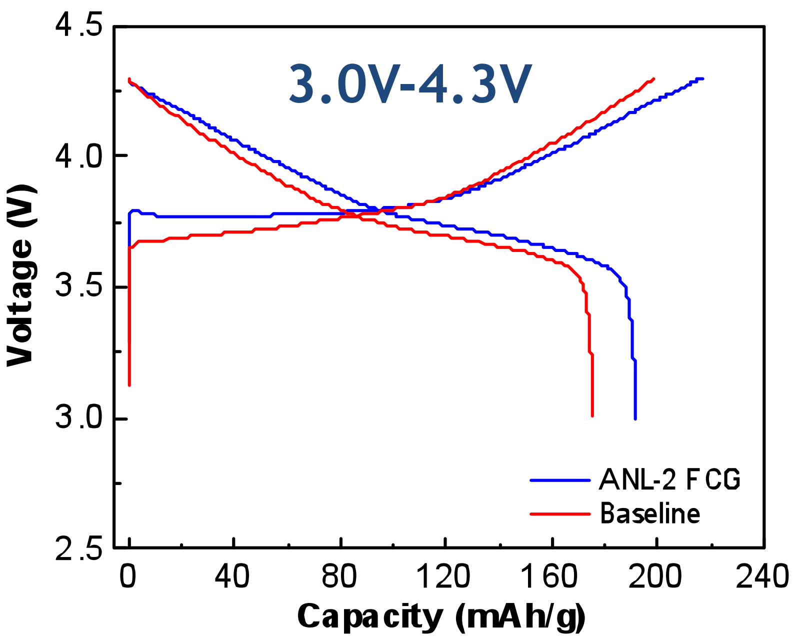
Precursors → Preheating T&t → Lithium amount → **Calcination T&t**

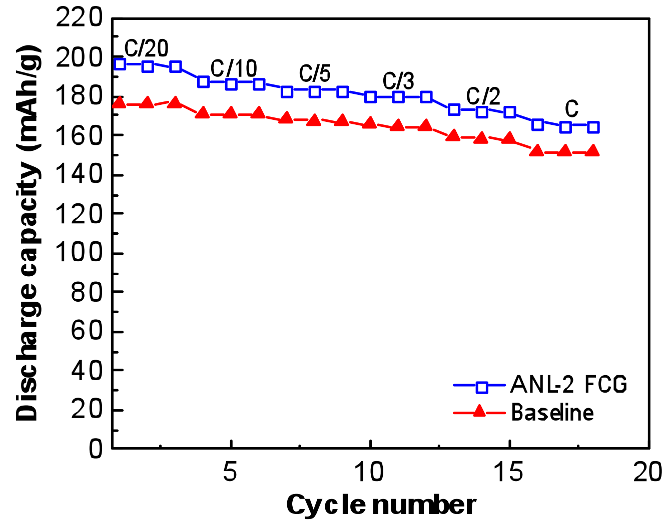


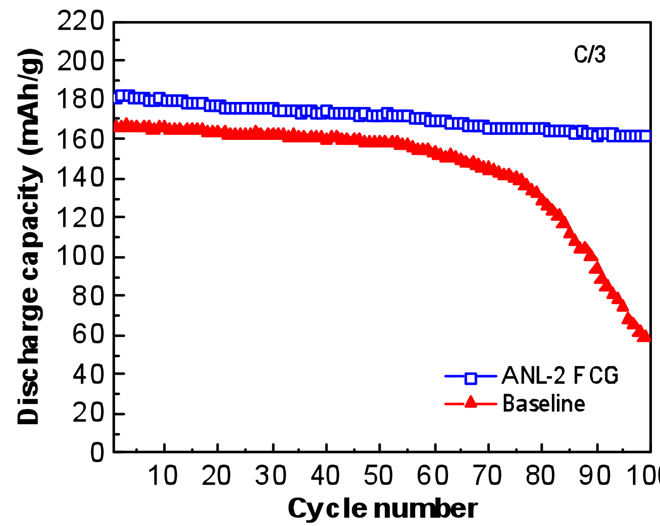
Calcination temperature and time of calcination have a great impact on cathode performance

Electrochemical performance of optimized FCG cathode

Half cell: Coinb cell 2032
Electrolyte: Gen 2, 1.2 M LiPF6 EC:EMC=3:7
Seperator: Celgard® 2325



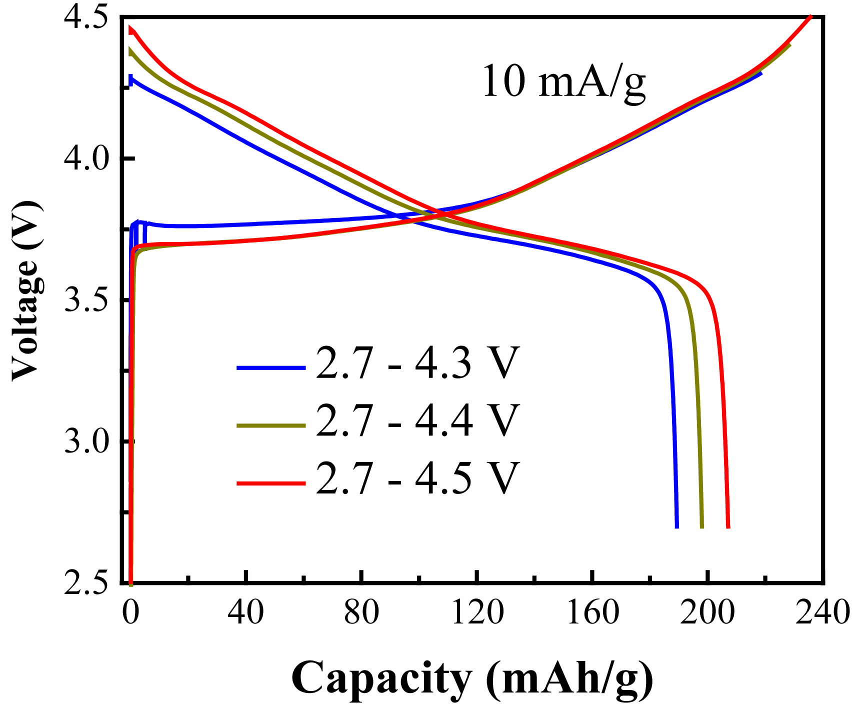


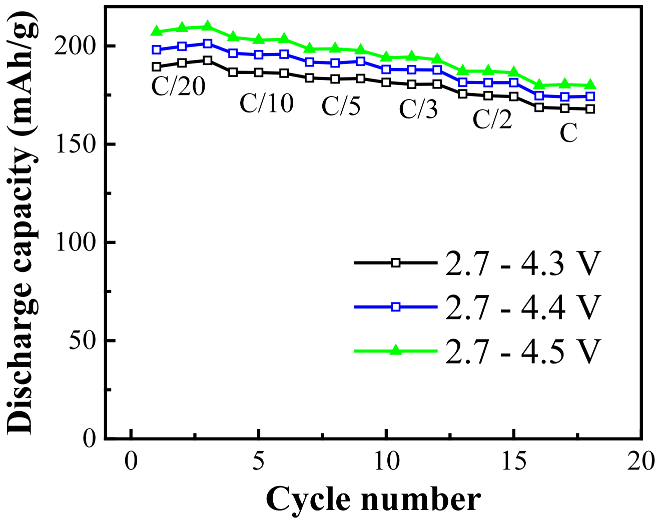


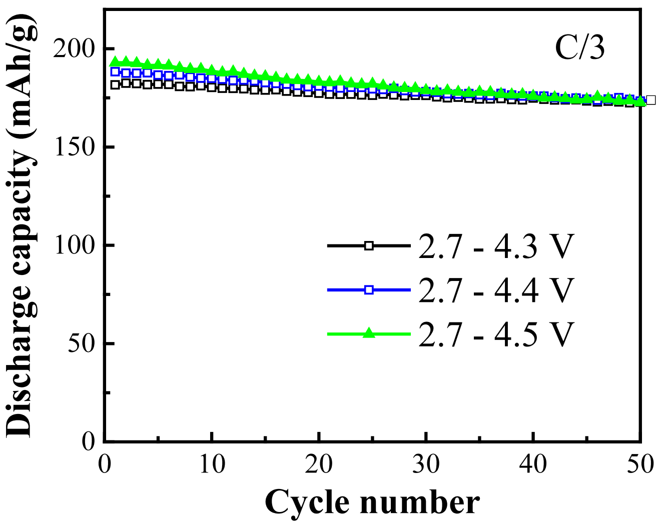
FCG (6:2:2) provides 192 mAh/g capacity with good stability at 4.3V compared to baseline NMC (6:2:2)

Electrochemical performance of FCG cathode at different cut-off voltages

- 2.7 – 4.3 V (192 mAh/g)
- 2.7 – 4.4 V (198 mAh/g)
- 2.7 – 4.5 V **(210 mAh/g)**

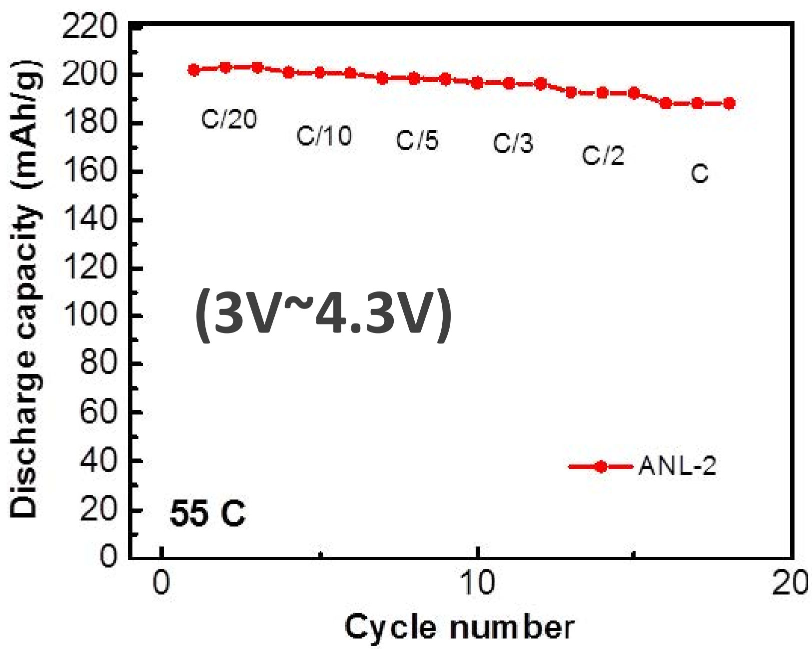


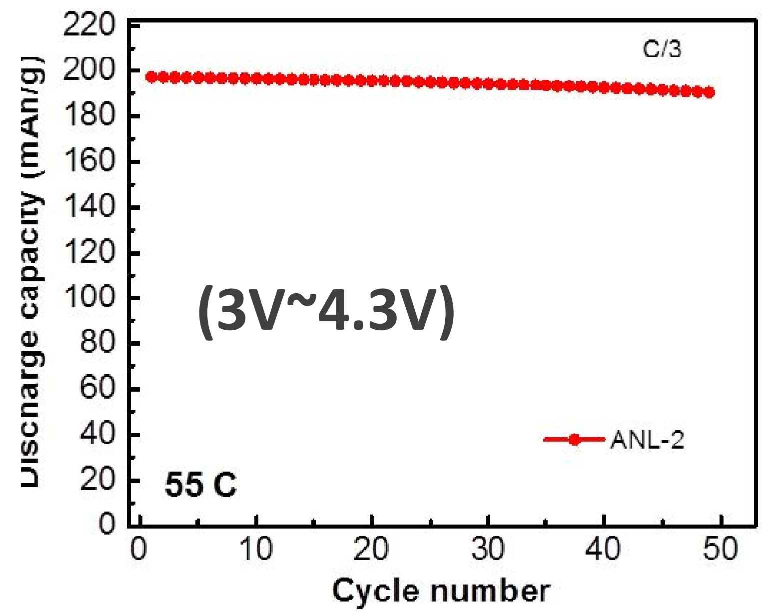




Electrochemical performance of FCG cathode at 55^{o}C

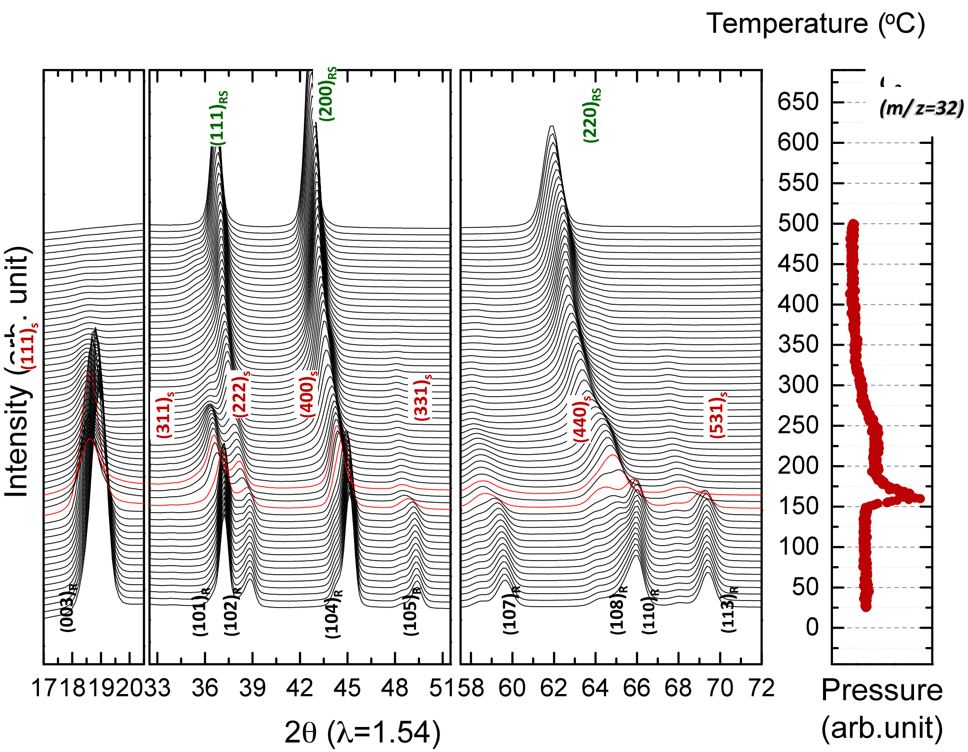
ANL-2 (FCG-6:2:2)



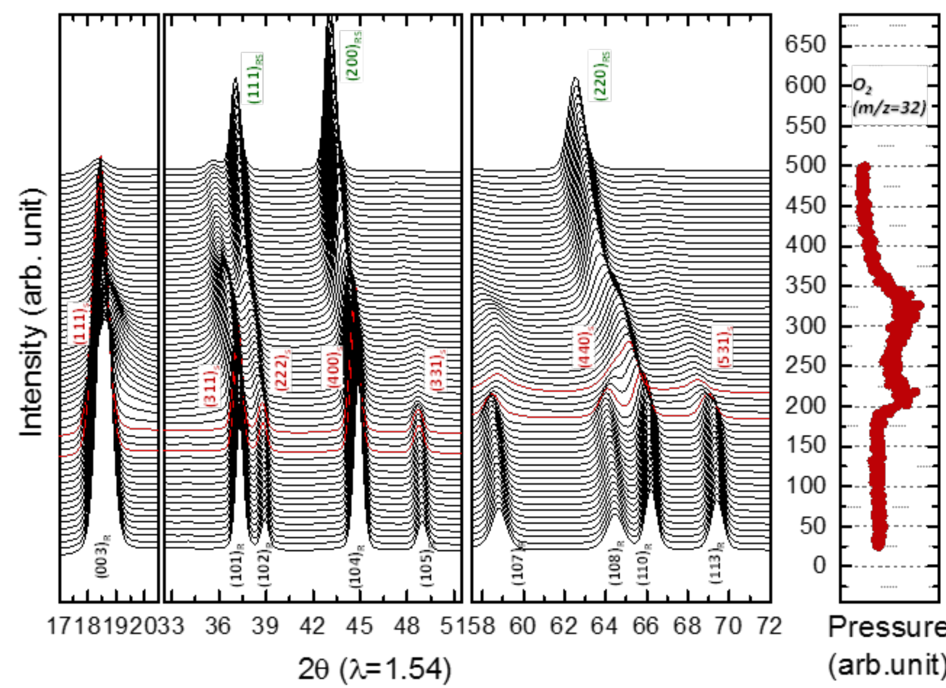


Excellent cycling stability at 55^{o}C

TR-XRD/MS of FCG (6:2:2) and NMC (6:2:2) baseline



$LiNi_{0.6}Mn_{0.2}Co_{0.2}O_4$ (Baseline NMC 622)

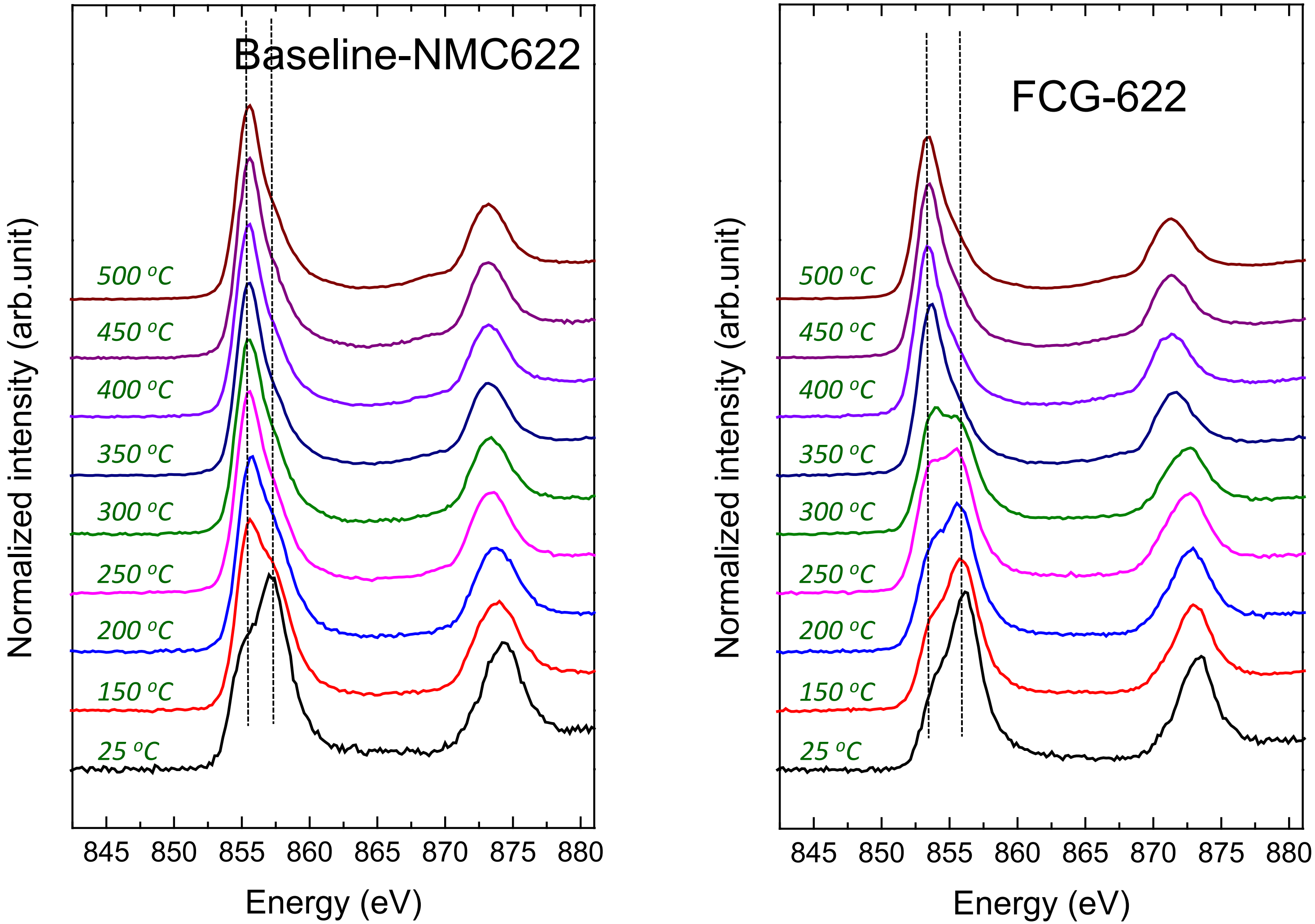


$LiNi_{0.6}Mn_{0.2}Co_{0.2}O_4$ (FCG-6:2:2))

- Sharp O_2 gas release (at *ca.* 150 °C) during phase transition from layered to disordered spinel phase

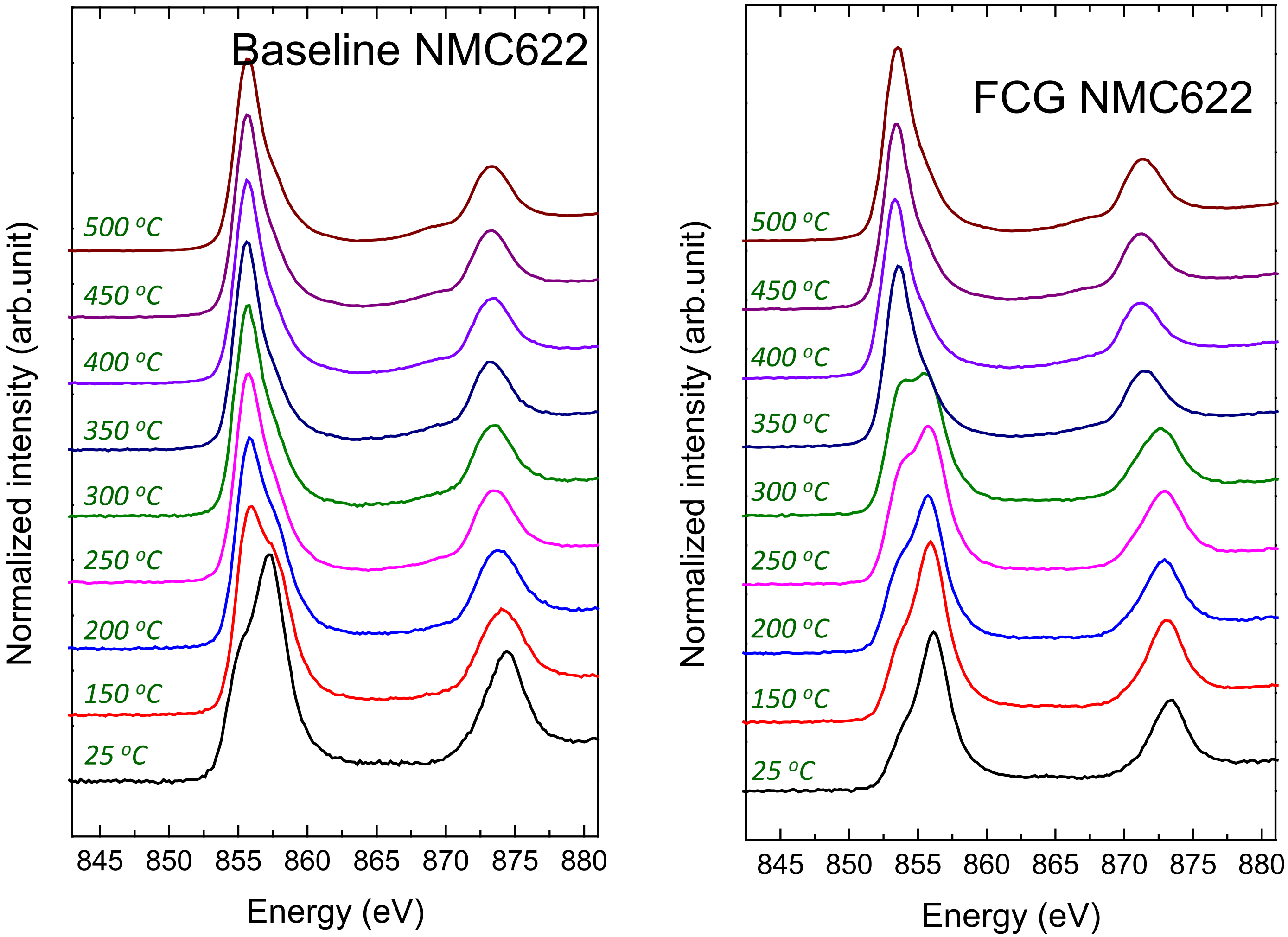
-Concentration gradient (FCG) sample shows much better thermal stability than baseline NMC 622
: 1st phase transition occurred at ca. 190°C

Ni L-edge soft XAS for baseline NMC622 (left) and FCG-622 (right) Using Fluorescence detection (FY, bulk probing)



Ni reduction reflected as the lower energy peak occurred quickly at low temperature (~150 °C) in baseline NMC622. In contrast, FCG-622 is more stable and Ni is stable up to 250 °C and gradually reduced, and completed at 350 °C

Ni L-edge soft XAS for Baseline NMC622 (left) and FCG (right) Using partial electron yield detection (PEY, Surface probing)

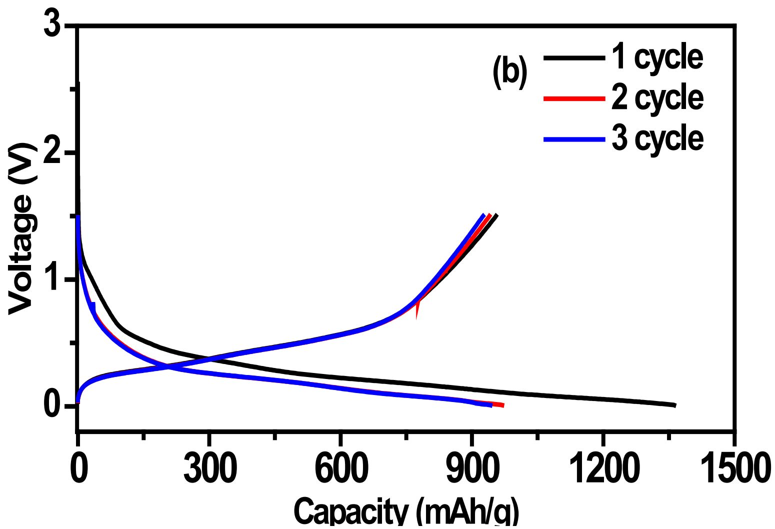


- The structural change at near surface also shows same trend with bulk structure.
- Ni reduction temperature is well coincident with the temperature of the phase transition and O2 release in TR-XRD/MS data

Optimization of SiO-SnCoC composite anode

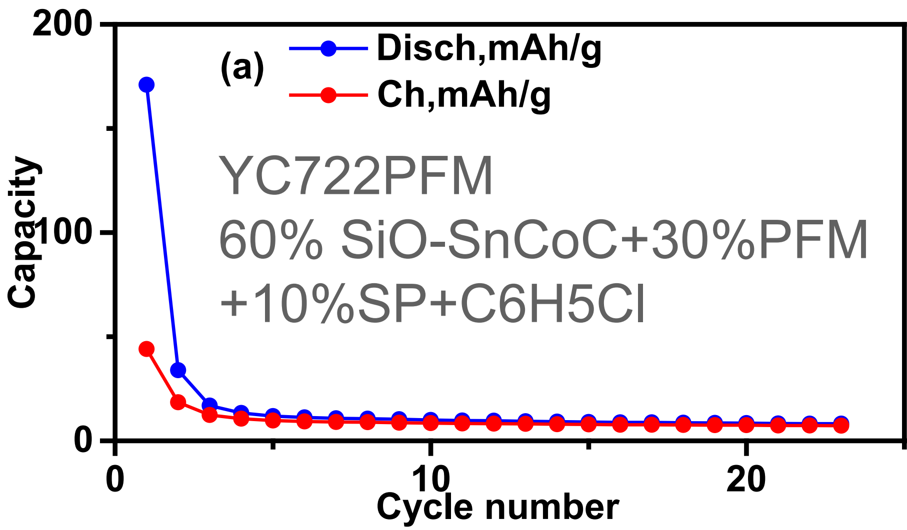
Main Issues:

Low efficiency: 65%~70%.



- Half cell SiO-SnCoC : 90/5%Timecal/5%PI
- Electrode loading: 2.5mg/cm^2
- 1st cycle reversibility between 70 to 72%.

Conductive binder (PFM) shows poor performance with Si-SnCoC composite



Approaches to resolving SiO-SnCoC composite anode issues

✓ Active material composition optimization:

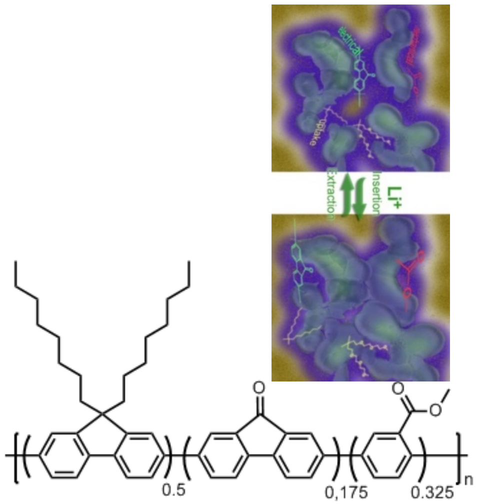
- Mixing appropriate amount of graphite with SiO-SnCoC
- Best composition based on graphite mixing optimization is:

(33%SiO-SnCoC +57% MAG graphite)

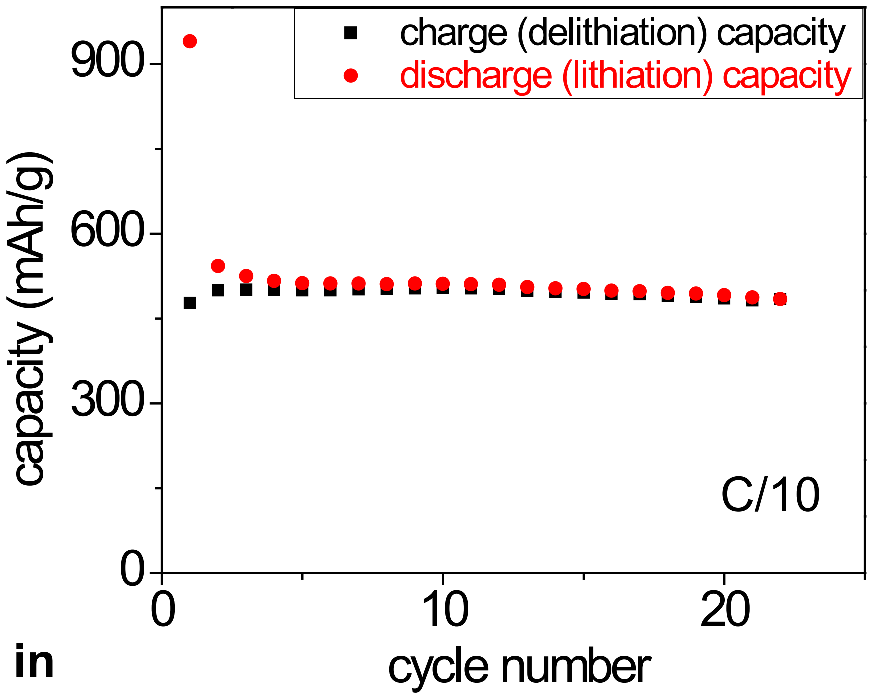
✓ Binder optimization:

- ✓ PFM conductive binder from LBNL
- ✓ PVDF
- ✓ Polyimide biner(PI)
- ✓ Polyacrylic acid binder (PAA)
- ✓ PVDF mix with PI
- ✓ PVDF mix with PAA
- ✓ LiPAA

Improvement of Performance of SiO-SnCoC mixed with 20% MAG graphite at C/10 half cell



Conductive binder

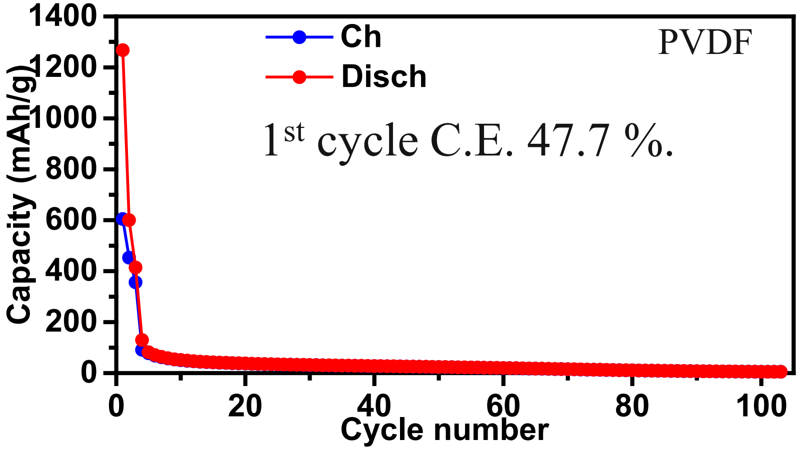


- **LBNL has made some progress in enabling their conductive binder with our SiOSnCoC/MAG composite anode**
- **First cycle efficiency is still very low (51%)**
- **Capacity of the composite anode is also low**

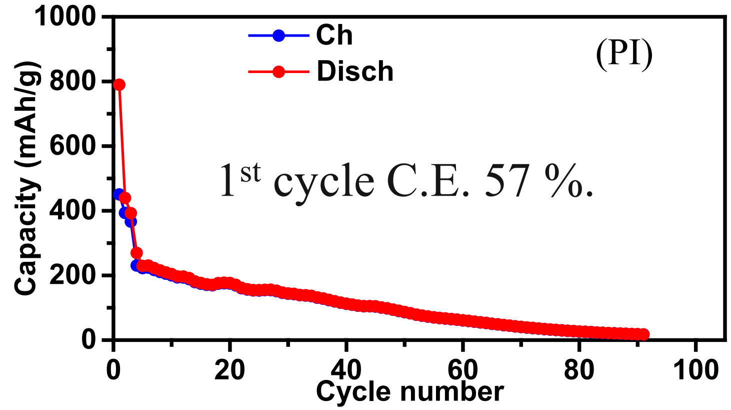
5% PFM,15% C-65, 60% SiOSnCoC, 20% MAG
Thickness: 76 µm
EC/DEC=3/7, 30% FEC, 1.2M $LiPF_6$
1st cycle efficiency: 51%, 22nd cycle efficiency: 99.9%

Effects of different binders on the cycling performance of electrode containing SiO-$Sn_{30}Co_{30}C_{40}$/MAG graphite

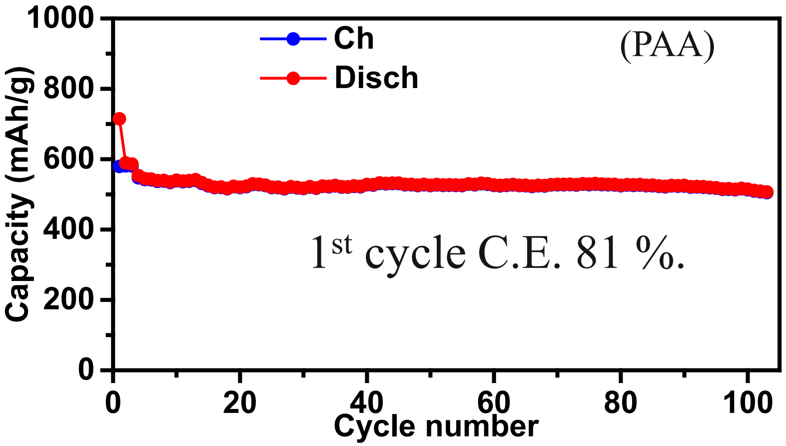
90% SiO-$Sn_{30}Co_{30}C_{40}$+4%C45+5%PVDF+1%PI



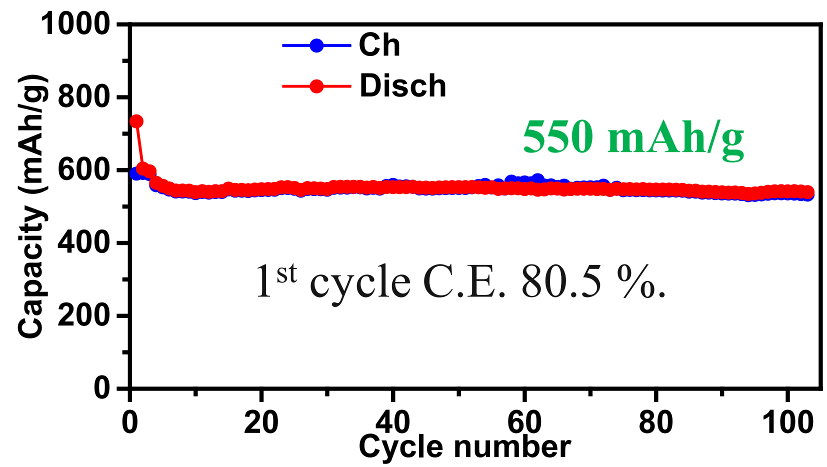
49.5% SiO-$Sn_{30}Co_{30}C_{40}$+49.5%MAG+1%PI



30% SiO-$Sn_{30}Co_{30}C_{40}$+60%MAG+
5%PAA+5%C-45

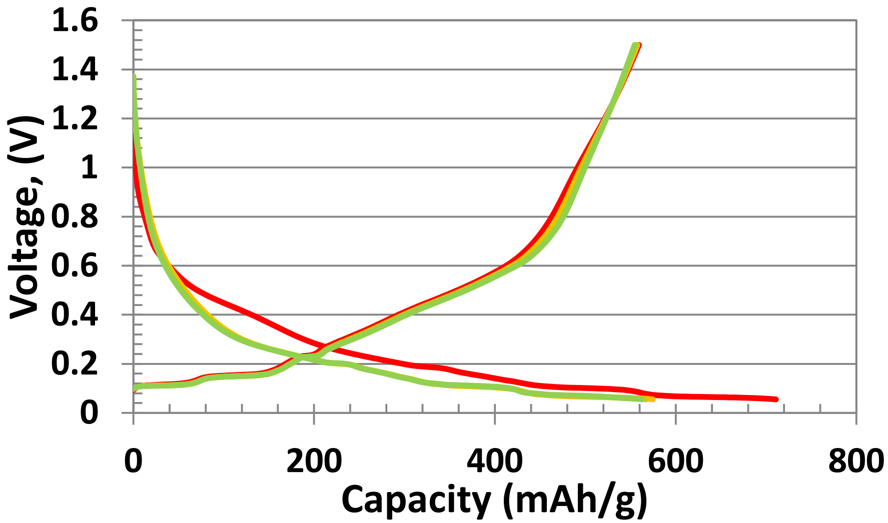


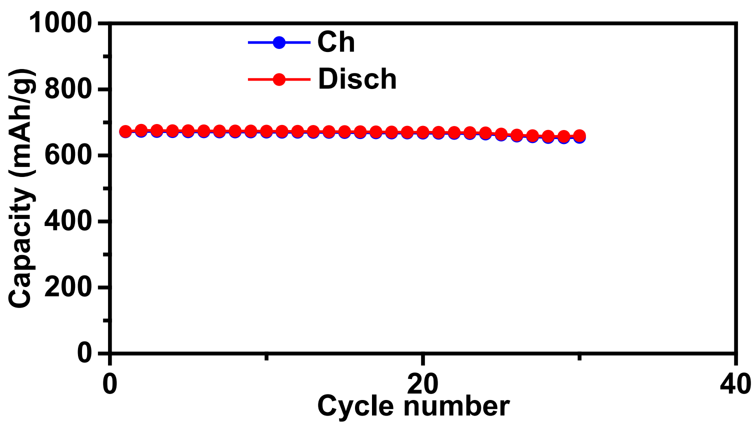
33% SiO-$Sn_{30}Co_{30}C_{40}$+57%Graphite+
4%LiPAA+5%C-45



33%SiO-$Sn_{30}Co_{30}C_{40}$/57%MAG graphite with 5%LiPAA shows the best performance with 81% 1st cycle efficiency

33% SiO-SnCoC+57%GC+5%LiPAA+5%C-45



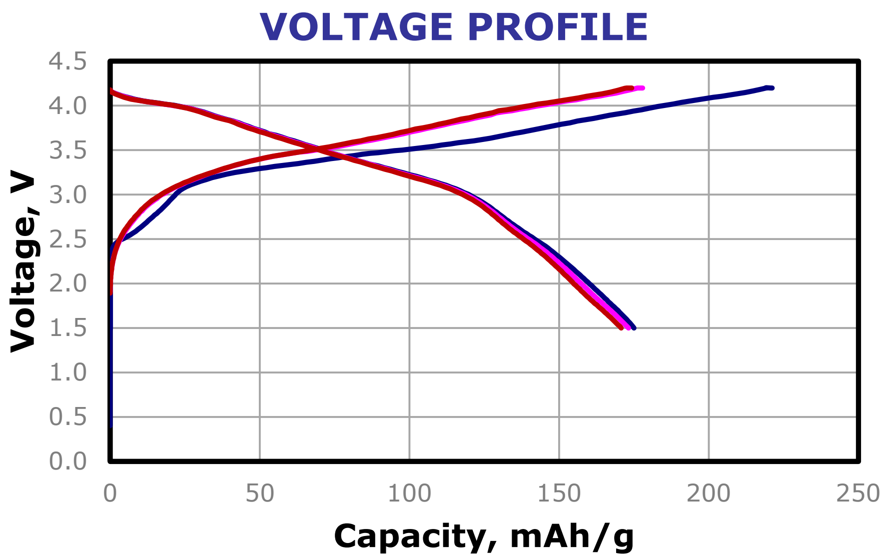


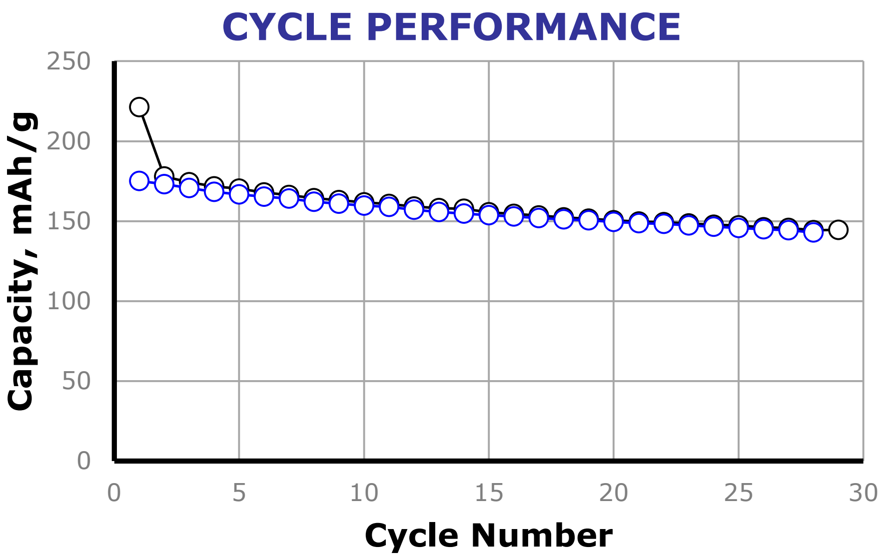
1st cycle C.E. 81 %.

1. The cell shows high 1st C.E. efficiency (81%).
2. The cell shows good rate performance.
3. The cell shows high capacity (670 mAh/g) and excellent cycle life so far.

33%SiO-$Sn_{30}Co_{30}C_{40}$/57%MAG graphite /5%LiPAA/ 5%C-45 formulation was used by CAMP facility to fabricate electrode for cell build

Initial performance of Full cell SiO-SnCoC-MAG/ FCG cathode

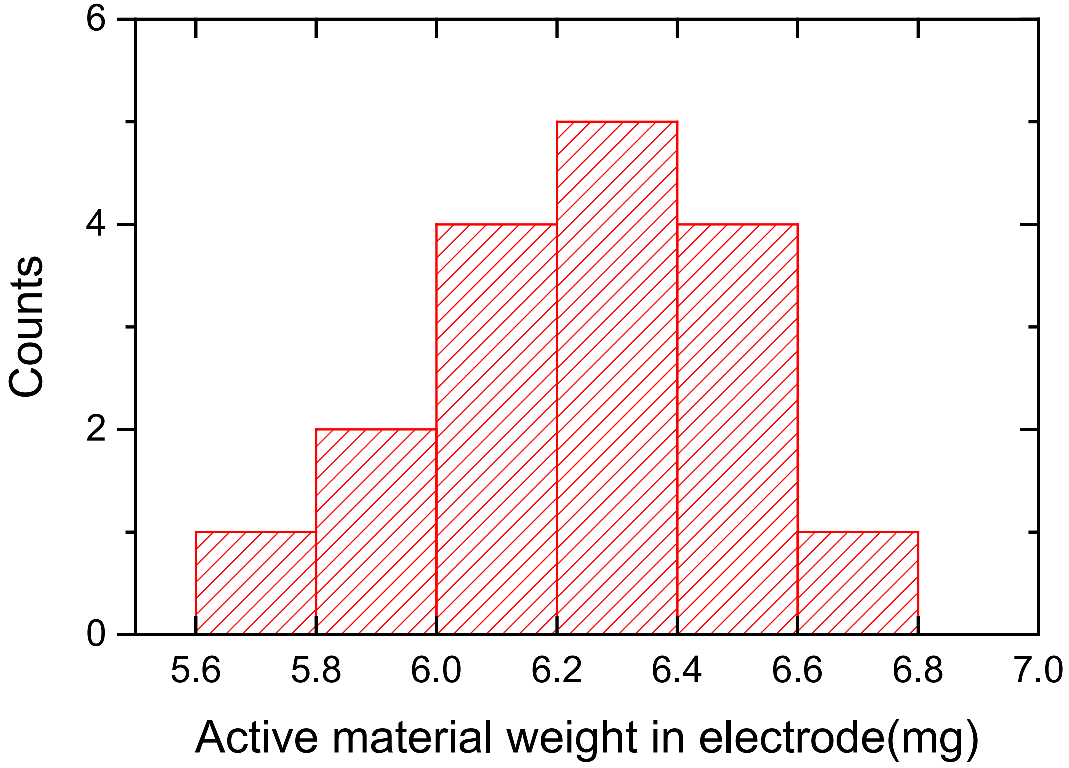




- **The first discharge capacity increases to 180 mAh/g with a high efficiency 79.1% which is almost the full efficiency of the anode.**

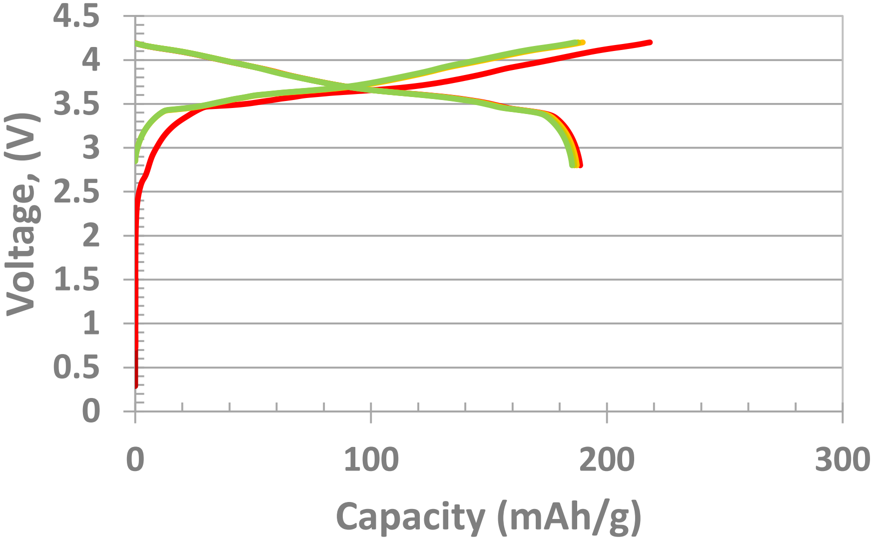
- **Cyclability of the cell is unsatisfactory even though both cathode and anode half cell shows excellent cyclability**

Poor Distribution of negative active material loading in the electrode is responsible for low cycle life in the full cell

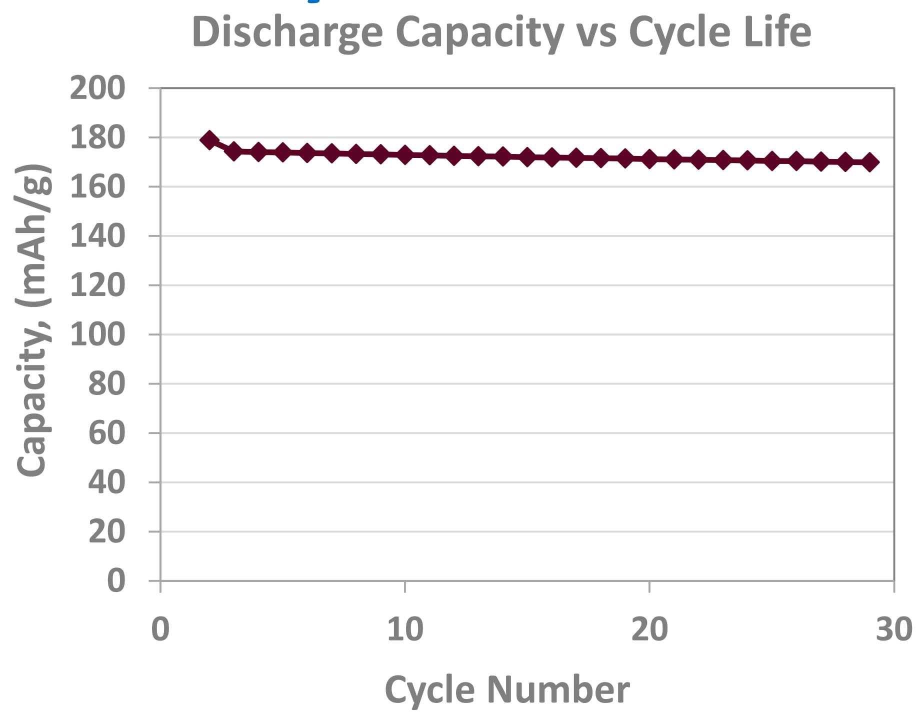


Negative active material loading made by CAMP shows varying distribution within the electrode; Possible reason could be 1) the particle size of the negative active material is not uniform and/ or 2) more time is needed to optimize the electrode processing at CAMP since this is a new material

Coupling FCG with Graphite instead of SiO-SnCoC-MAG shows excellent cycle life



1st C cap (mAh/g)	**218**
1st D Cap (mAh/g)	**189**
1st Cycle Eff (%)	**86.5**



By replacing SiO-SnCoC-MAG composite with graphite, the cycle life of the full cell with FCG cathode improved significantly, confirming the observed uniformity issue of our SiO-SnCoC-MAG composite during the electrode making process at scale.

Energy and power of baseline and FCG cells based on BatPac Design

Deliverable	Device	Battery Performance (Cell Level)			
		Usable Specific Energy (Wh/kg)	**Energy Usable Density** (Wh/l)	**Power at SOCmin** (W/kg,10sec)	**Technology Info**
***Baseline**	**20Ah Cell** **40Ah Cell** BatPac Design	**(~199)** **(~237)**	**(~453)** **(~548)**	**(~1591)** **(~950)**	SiO-SnCoC And NMC (6:2:2)
Gen1	**20Ah Cell** **40Ah Cell** BatPac Design	**(~229)** **(~280)**	**(~541)** **(~659)**	**(~1837)** **(~1120)**	SiO-SnCoC-MAG And FCG (6:2:2)

*** Data provided on baseline last year was higher than the one in the table above as we found a mistake in the Pat Pac model input.**

Responses to Previous Year Reviewers' Comments

- Question: Reviewer 7 has a question regarding the synthesis of FCG. The reviewer misunderstood our process. the reviewer believe we use a continuous process which require reaching a steady state!
- Answer: The FCG material was made using a batch process! The reaction starts from half full reactor, and end when the reactor is full. All the materials are collected as FCG precursor. The process is easy to control and to scale up

- Question : The reviewer No:4 question the alloying of Sn and Si
- Response: since the material is amorphous , it is difficult to carry out bulk characterization. The alloying assumption was based on the PDF result only.

- Question: Reviewer 5 would like to see full cell evaluation using cylindrical cells
- Response: since the project was new and started only few months before the AMR review, it was not possible to carry out cell evaluation using 18650 size cell. The project anticipate making full cell with gradient and Si-composite once optimized at the end of the project. the 1st cycle efficiency of our Si-Sn composite (55%) was significantly improved by incorporating MAG graphite to the system (81%) see page 20 of this presentation.

Responses to previous year reviewers' comments

- Question: Reviewer 6 has a question regarding the rate capability of FCG cathode and third party validation.
- Answer: The FCG material shows very good rate capability (see Fig 10 & 11) of this presentation. It is our plan to deliver full pouch cell to INL for validation by late June of this year.

- Question: reviewer 6 want to see data beyond proof of concept. He want full cell build and tested and he request doing some cost analysis
- Response: our plan was to build full pouch cell data based on the optimized FCG and Si-Sn-MAG graphite anode with high efficiency by late June of this year and carry out all the test requested by the reviewer. We are planning to send cells to INL for independent testing. The cost analysis will be made on the final optimized cell.

- Question: the reviewer 7 didn't not believe that FCG material meet the target value
- Response: The BatPac model shows that FCG coupled with Si-Sn-MAG graphite can provide up 280Wh/kg (see page 24) which is higher than the 200Wh/kg targeted by DOE

Collaborations

- X.Q. Yang of BNL
  - Diagnostic of FCG and SEI of Si-Sn composite electrodes using soft & hard X-ray.

- G. Liu (LBNL)
  - Development and optimization of conductive binder for Si-Sn composite anode

- H. Wu (ANL)
  - Optimize the synthesis of FCG cathode

- A. Abouimrane (ANL)
  - Development of $SiO\text{-}Sn_yCo_{1-x}Fe_xC_z$ anode

- J.Lu & Z. Chen (ANL)
  - Characterization of cathode, anode and cell during cycling using In-situ techniques

- ECPRO : Baseline cathode material

- University of Utah : Facility to scale up the baseline Si-Sn composite anode for baseline cell

- A. Jansen & B. Polzin (ANL)
  - Design & fabrication of baseline cell

Proposed Future Work for Fy 2015 and FY 2016

- FY 2015 Q3 Milestone:
  - Optimize the electrode processing of SiO-SnCoC-MAG to get uniform electrodes
  - Demonstrate up to 500 cycles of SiO-SnCoC-MAG using new LiPAA binder
- Fy 2015 Q4 Milestone:
  - Improve further FCG cathode capacity to 220~230mAh/g at high voltage 4.4V and 4.5V trough particle coating with AlF_3
  - Demonstrate 250wh/kg at the cell level using improved FCG cathode and SiO-SnCoC-MAG anode .
- FY2016 work proposed
  - Finalize the optimization of conductive binder
  - Finalize the optimization of FCG with 230mAh/g
  - Optimize and build pouch cell based on SiO-SnCoC-MAG with conductive binder and AlF_3-coated FCG and carry out testing and validation

Summary

- **Relevance**
  - enable low battery cost by increasing energy density
  - Low battery cost will lead to mass electrification of vehicle and reduction of both greenhouse gases and our reliance on foreign oil
- **Approaches**
  - develop very high energy redox couple (250wh/kg) based on high capacity full gradient concentration cathode (FCG) (230mAh/g) and Si-Sn composite anode (670mAh/g) with long cycle life and excellent abuse tolerance to enable 40 miles PHEV and EVs
- **Technical Accomplishments**
  - Optimize the process of making FCG cathode and demonstrate capacity as high as 210mAh/g with 2.7 tap density
  - Scale up FCG cathode to 1Kg level for electrode making using CAMP facility at Argonne
  - Improve the efficiency of $SiO\text{-}Sn_{30}Co_{30}C_{40}$ anode to 81% by Developing $SiO\text{-}Sn_{30}Co_{30}C_{40}$ –MAG graphite composite formulation and scale up the new composite to 1Kg level.
- **Proposed Future work**
  - Optimize the electrode processing of SiO-SnCoC-MAG to get uniform electrodes
  - Demonstrate up to 500 cycles of SiO-SnCoC-MAG using new LiPAA binder
  - Improve further FCG cathode capacity to 220~230mAh/g at high voltage 4.4V and 4.5V trough particle coating with AlF_3
  - Demonstrate 250wh/kg at the cell level using improved FCG cathode and SiO-SnCoC-MAG anode .